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ATMOSPHERIC RADIATION,  
OPTICAL WEATHER, AND CLIMATE

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## Surface Ozone in the Atmosphere of Moscow during the COVID-19 Pandemic

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**Abstract**—We present the results from monitoring surface ozone in the atmosphere of Moscow in 2020 and 2021 under lockdown conditions linked to the COVID-19 pandemic. These two years significantly differed in meteorological conditions and the level of anthropogenic environmental load. A level of surface O<sub>3</sub> concentrations, relatively low for a megalopolis, was observed in Moscow in 2020. The annual average concentration was 28 μg/m<sup>3</sup>, and the annual maximal concentration was 185 μg/m<sup>3</sup>. That was due to relatively cool summer with the low content of pollutants in atmospheric air. Intense heat waves were observed in the megalopolis during summer 2021 under the conditions of a blocking anticyclone, when the daytime temperatures rose to 35°C. Combined with higher atmospheric air pollution, this resulted in unusually high O<sub>3</sub> concentrations. The annual average concentration was 48 μg/m<sup>3</sup>, and the annual maximal concentration was 482 μg/m<sup>3</sup>.

**Keywords:** atmosphere, air, surface ozone, maximum permissible concentration, surface layer, troposphere, ozone precursors, COVID-19 pandemic, lockdown

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### INTRODUCTION

Surface ozone is an important chemical constituent of the Earth's atmosphere, playing a significant role in forming its oxidation potential [1, 2]. In turn, oxidation of both organic and inorganic substances is one of the main components in the cycle of substances in nature [2].

Surface ozone strongly affects living organisms. The nonpolluted atmosphere contains a minor (as low as 30 μg/m<sup>3</sup>) background ozone amount. At these concentrations, ozone affects living organisms as a soft mutagenic and tonic factor, allowing them to adapt to environmental changes and keep evolving [3–8]. Introduced into the human body as an aqueous solution, ozone may have immunomodulatory, anti-inflammatory, antibacterial, antiviral, and antifungal effects [9].

At high concentrations observed during strong pollution of atmospheric air in big cities and industrial regions and exceeding accepted sanitary standards (daily average maximum permissible concentration (MPC<sub>d.a</sub>) is 30 μm/m<sup>3</sup>, and the one-time maximum permissible concentration (MPC<sub>m.o</sub>) is 160 μg/m<sup>3</sup>), ozone has pathogenic properties [10–14]. Being a

strong oxidant, ozone is harmful to the respiratory organs and causes a systemic inflammation of blood circulating organs. Increased ozone content in the surface atmosphere is considered to cause not only a stronger morbidity of the respiratory organs, blood circulating organs, and nervous system, but also greater total mortality [15–17]. Increased surface ozone content also adversely affects the ecosystems, forests, individual plants, and productivity of certain agricultures [18, 19].

In the clean surface atmosphere, ozone is generated via the cycle of photochemical reactions with the participation of nitrogen oxides and solar UV radiation; conversely, ozone is destroyed after being chemically bound to nitrogen monoxide (NO) or subject to dry deposition [1, 2]. In the atmosphere polluted by the products of incomplete combustion (carbon monoxide, volatile hydrocarbons), the process of ozone binding to NO is slowed down, and the ozone generation rate may have been much larger than the rate of ozone destruction. In this case, ozone is accumulated and its concentration increases in the surface air layer. The ozone generation rate also strongly increases with rising temperature [1, 2]. The ozone content in the surface layer depends on air humidity, the intensity of

wind-driven air-mass-mixing processes, destruction and sink upon the interaction with the Earth's surface, vegetation, and soil.

Increased surface ozone concentrations (SOCs) present the largest problem in big cities and industrially developed southern regions, such as North America, southern European countries, and China, where there are large anthropogenic environmental loads and a hot climate. In Russia and, in particular, in Moscow, high ozone concentrations were first recorded in the surface atmosphere in two recent decades [20–24]. First, this is because motor vehicles have rapidly grown in number, producing more exhaust emissions to the atmosphere; second, this is due to ongoing climate change, which resulted in regular heat waves with daytime temperatures of up to 35–40°C in Central Russia.

In 2020 and 2021, a unique situation developed in the air basin of the Moscow region, making it possible to estimate the effect of both high temperatures and gaseous pollutants on the ozone generation rate and its accumulation in the surface atmosphere.

The COVID-19 pandemic began in 2020; therefore, “high alert measures” and lockdown were imposed in Russia in March. As in the neighboring European countries and China, Russia rapidly reduced economic activities as well as the intensity of road and air traffic. A simultaneous compliance with the strict lockdown measures in many countries has led to a marked reduction of pollutant emissions to the atmosphere around the globe, which was recorded by many atmospheric air quality monitoring facilities [25–27]. It is noteworthy that the events with anomalous (both too high [33, 34] and too low [35–37]) ozone levels in the surface atmosphere were also reported [28–32]. After strict lockdown measures were imposed, we, too, recorded the effect of SOC reduction at the surface ozone monitoring station, located in background plain region in Central Russia in Vyatskiye Polyany, Kirov oblast [37, 38]. At this station in late March, i.e., just after the high-alert announcement in Russia, there was a jump-like three-fold reduction of SOC values, both monthly average nighttime minima and daytime maxima. The traditional springtime TOC maximum in April was weakly pronounced at this station. These results indicate not only a local, but also a global reduction of surface ozone.

The year 2021 turned out to be unusual in terms of meteorological conditions. The pandemic-linked restrictions in Moscow were relaxed, so that pollutant concentrations in the atmosphere returned to the previous level. At the same time, spring and summer in Central Russia were warmer and dryer than usual, owing to the specific features of large-scale air circulation that created the conditions for both anomalously high temperatures and for pollutant accumulation in the surface air layer [39, 40]. Thus, the years 2020 and 2021 in the Moscow region strongly differed in mete-

orological conditions and in the level of anthropogenic load on the atmosphere.

The purpose of this work is to compare the long-term SOC behaviors, recorded at the center of Moscow at the RUDN monitoring station in 2020 and 2021, and to clarify the role the temperature and the concentration of gas pollutants play in ozone generation under megalopolis conditions.

## INSTRUMENTS AND METHODS

The data for analysis were acquired at the station for monitoring surface ozone, ozone precursors, and the main meteorological parameters; the station started to operate at the Peoples' Friendship University of Russia with participation of Prokhorov General Physics Institute, Russian Academy of Sciences, in late 2019. The station is located at the center of Moscow within the Third Ring Road in Ordzhonikidze Street (55°42'37" N, 37°36'78" E, 149 m ASL). The station is surrounded by urban residential buildings, as well as by a few parks and boulevards. The nearest highways, which are the main sources of ozone precursors, are more than 1 km away from the station. There are no industrial structures nearby.

In addition to measurements of the O<sub>3</sub> concentration, the station also monitors NO, NO<sub>2</sub>, CO, CH<sub>4</sub>, and hydrocarbons and measures the mass concentrations of aerosol particles of different sizes and the main meteorological parameters. A 3-02P chemiluminescent gas analyzer, developed and manufactured by the Instrument-Making Enterprise OPTEC (St. Petersburg) and awarded the international certificate from U.S. Environmental Protection Agency [41, 42], is used for ozone measurements. The main metrological characteristics of the analyzer are: the dynamic range is 0–500 µg/m<sup>3</sup>, the sensitivity is 1 µg/m<sup>3</sup>, the error limit is 15%, the integration time is 1 min, and the recording rate is once a minute. To reduce the measurement error, the instrument is automatically calibrated every 10 min using a calibration gas mixture or “null gas.” The manufacturer tests and calibrates the instrument once a year using the first-rank working standard of the ozone molar fraction unit in ozone–air mixtures RE 154-1-33-2008, which is stored in the OPTEC instrument-making enterprise. The gas analyzer is operated as a part of automated measurement complex, ensuring data acquisition, storage, preliminary processing, and transfer, as well as data display and remote control. The air intake is carried out in the inner yard of the RUDN buildings at an altitude of ~5 m via standard Teflon samplers. The measurements are carried out in the continuous long-term monitoring mode. The current parameters are measured once a minute and stored in the database at the measurement complex.

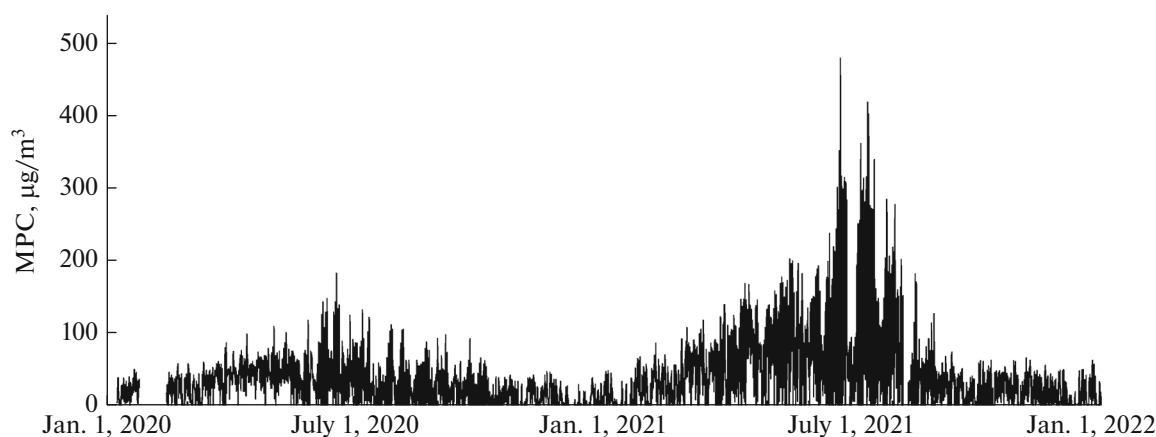


Fig. 1. Time behavior of SOC at RUDN station, Moscow.

### OZONE MONITORING IN THE SURFACE ATMOSPHERE

We monitored the surface ozone continuously for 2020 and 2021.

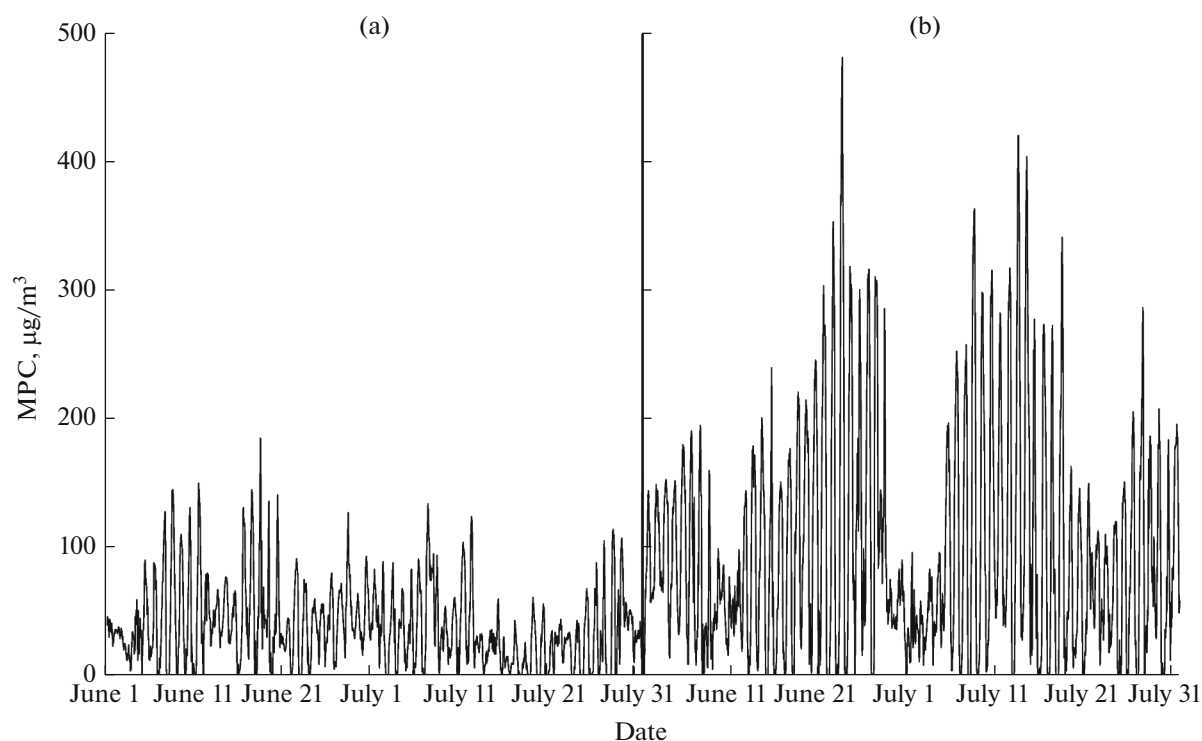
Figure 1 shows the time behavior of the hourly average SOC recorded for these two years. We can clearly see two annual cycles of variations in the ozone concentration caused by the annual cyclicities of temperature, illumination, and daytime length. The surface ozone concentrations are minimal at low temperatures and during short days. The annual behavior of SOC is very typical for the atmosphere of a megalopolis. The growth of daytime temperatures during winter is accompanied by the SOC increase. The SOC reaches maxima in summer, in June or July. SOC starts gradually decreasing in August under the conditions of diminishing daily average temperatures and shortening daytime. It can be seen that the ozone content strongly varies in time during the year. The SOC can vary from zero to maxima within quite short (a few hours) periods of time; therefore, the annual behavior look like “noisy” random fluctuations.

The maximal SOC in Moscow were no more than  $180 \mu\text{g}/\text{m}^3$  in late June 2020; while in 2021, SOC were anomalously high. A monotonic SOC growth has been apparent as early as March. In April, the daily average concentrations reached  $100 \mu\text{g}/\text{m}^3$  and more, much larger than  $\text{MPC}_{\text{d.a}}$ ; and the daily maximal hourly concentration started regularly exceeding  $\text{MPC}_{\text{m.o}}$ . The photochemical ozone generation in the surface atmosphere intensified in mid-March, so that the daily maximal concentrations exceeded  $200 \mu\text{g}/\text{m}^3$  every day. The SOC in the Moscow atmosphere were extremely high in June after passage of three heat waves. In that time, the weather was determined by a stable blocking anticyclone conducive to conditions, on the one hand, for anomalously high temperatures and low humidity and, on the other hand, for pollutant accumulation in the surface atmosphere [39, 40]. It is noteworthy that,

for a few days, the daily maximal temperatures reached  $35^\circ\text{C}$ , while nighttime temperatures did not decrease to below  $25^\circ\text{C}$ . In daytime hours, it was dry, the relative humidity decreased to below 35%, the atmospheric pressure reached 758 mmHg, and wind blew from predominantly southwestern directions at a speed of up to 2 m/s. In nighttime hours, the wind changed the direction to southeast and calmed down. These conditions were ideal for intense photochemical ozone generation and ozone accumulation in daytime hours. For more than 40 days, from mid-June to mid-August, SOC in excess of  $160 \mu\text{g}/\text{m}^3$  were observed from 06:00 to 10:00 LT. The heat waves, lasting for 10–14 days, were followed by short periods of rainy weather, when the maximal daytime SOC decreased to  $\sim 100 \mu\text{g}/\text{m}^3$ . A characteristic feature of the daily cycle of surface ozone in megalopolises during the spring–summer period is that the nighttime ozone concentrations were close to zero independent of how large the daytime concentrations were (Fig. 2). This trait, stemming from the relatively high NO content in the Moscow atmosphere at night, had been regular throughout summer 2021.

For comparison, Fig. 2, on an enlarged scale, shows ozone variations in those 2020 and 2021 periods, when the largest SOC were recorded.

Several most important features of the SOC time variations can be noted. First, we can clearly see the abovementioned wavelike character of daytime SOC, alternating between high- and moderate-concentration periods. Figure 2a (2020) shows two waves of minor increase in SOC; and Fig. 2b (2021) shows two waves, which were most intense in that year, and during which SOC reached a maximum of  $\sim 482 \mu\text{g}/\text{m}^3$ . Second, we can clearly see the circadian rhythm of the time variations in the SOC, associated with alternating day and night. SOC are very low (high) in nighttime (daytime) hours. Thus, the variations, “noisy” in character, become regularly periodic after a more careful inspection. The presence of circadian SOC rhythm



**Fig. 2.** Variations in hourly average SOC in the periods of maximal levels in June–July of (a) 2020 and (b) 2021 at RUDN station.

makes it possible to average and accumulate the data over the day, which was found to be more informative than a simple sequential data smoothing. This approach is widely used to analyze both daily SOC variations and long-term SOC trends [1, 17, 20, 22–24, 43].

Figure 3 presents the daily variations in SOC and temperature after seasonal averaging. They are obtained after hourly summation and a subsequent normalization of the daily variations of these parameters in each season. It can be seen that, despite the fact that the temperature was, on average,  $\sim 5^{\circ}\text{C}$  lower during winter 2021 than in 2020, the wintertime daily SOC variations differ little between 2020 and 2021. This can be because the photochemical ozone generation is minor at low winter temperatures, so that this difference in the average temperatures does not markedly affect the daytime ozone production.

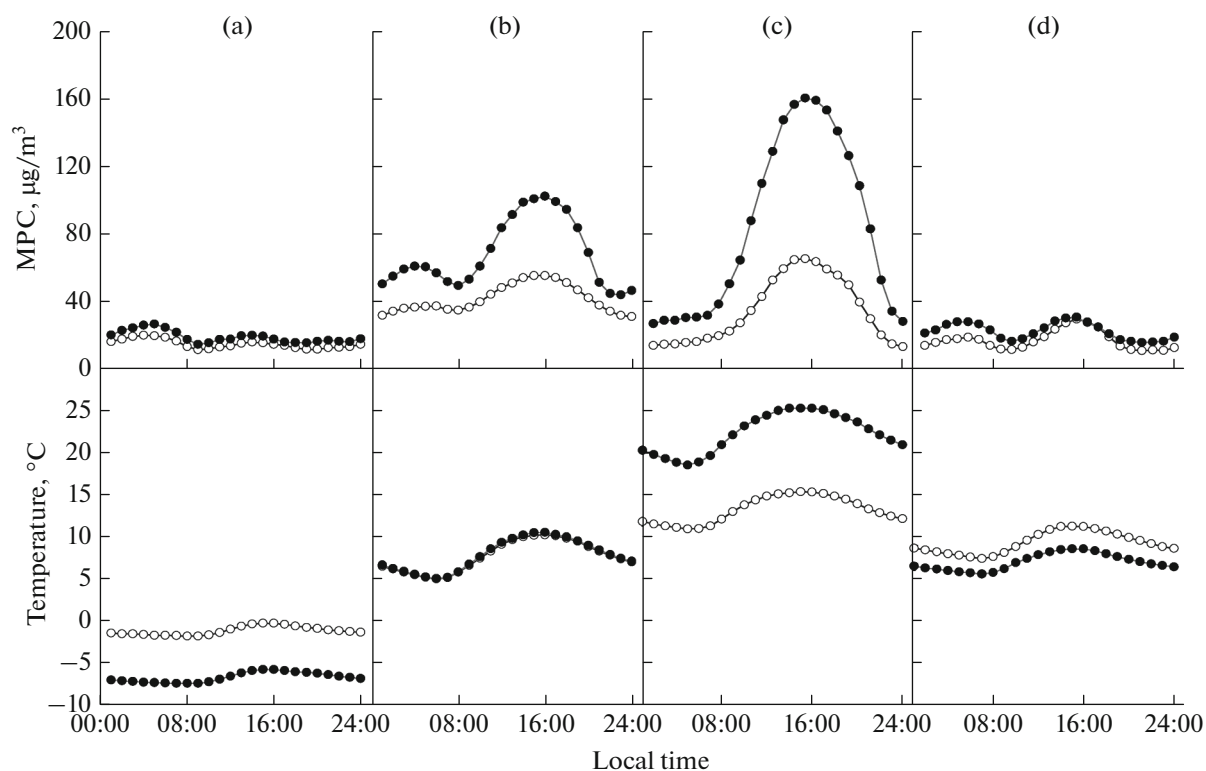
The spring average temperature variations coincided in 2020 and 2021. At the same time, the amplitude of the daytime SOC maximum turned out to be almost a factor of two larger, and the daytime SOC increment (the difference between the daytime maximum and nighttime minimum) turned out to be almost a factor of three larger in spring 2021 than in 2020. That difference could be because air in the megacropolis was polluted by nitrogen oxides, carbon monoxide, and volatile organic compounds weaker in spring 2020 during the COVID-19 pandemic; as a consequence, less ozone was produced in daytime in

2020 than in 2021 under nearly identical temperature regimes.

As is already mentioned above, summer 2021 was hot, with the summer average daily variations in the temperature lying  $\sim 10^{\circ}\text{C}$  higher than that for 2020. The difference in the summer variations in the daily SOC between 2020 and 2021 is even more contrasting. Considering that the atmosphere was differently polluted in springs 2020 and 2021, the increase in SOC during summer 2021 can be attributed to the joint effect of higher temperatures and stronger pollution of Moscow air by ozone precursors.

Despite the small difference in the averaged temperatures, the daily variations in SOC differ little between 2020 and 2021, which, as in the winter period, can be because the photochemical ozone production is weakly effective.

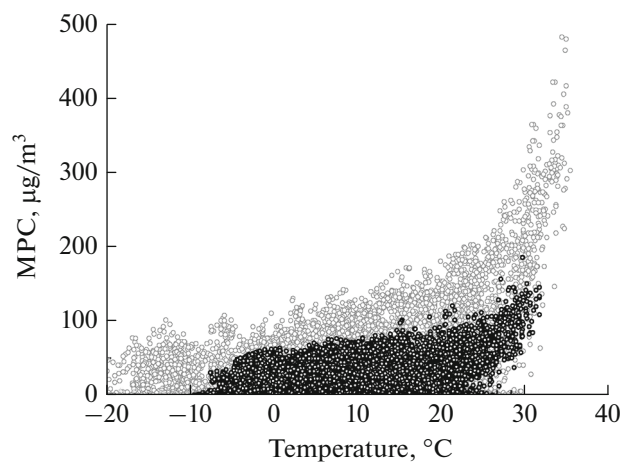
The joint effect of increased temperature and ozone precursor concentrations on the SOC levels can be clearly seen on the distribution diagram of the hourly average SOC as functions of the atmospheric air temperature (Fig. 4). This diagram accurately characterizes the difference in the temperature conditions between these years. The temperature varied in the ranges from  $-10$  to  $+32^{\circ}\text{C}$  in 2020 and from  $-20$  to  $+35^{\circ}\text{C}$  in 2021. It can be seen that SOC quite weakly depends on the temperature when the latter is below  $+10^{\circ}\text{C}$ . A sharp exponential [1, 2] dependence becomes marked above  $+20^{\circ}\text{C}$ . It is noteworthy that



**Fig. 3.** Daily variations in SOC and temperature in 2020 (open circles) and 2021 (closed circles) at the RUDN station in (a) winter, (b) spring, (c) summer, and (d) fall.

the SOC values recorded in 2020 are below those recorded in 2021 for all temperatures. The SOC variability ranges show a twofold difference up to  $+20^{\circ}\text{C}$ . This difference rapidly increases above  $+20^{\circ}\text{C}$ , until becoming threefold above  $+30^{\circ}\text{C}$ .

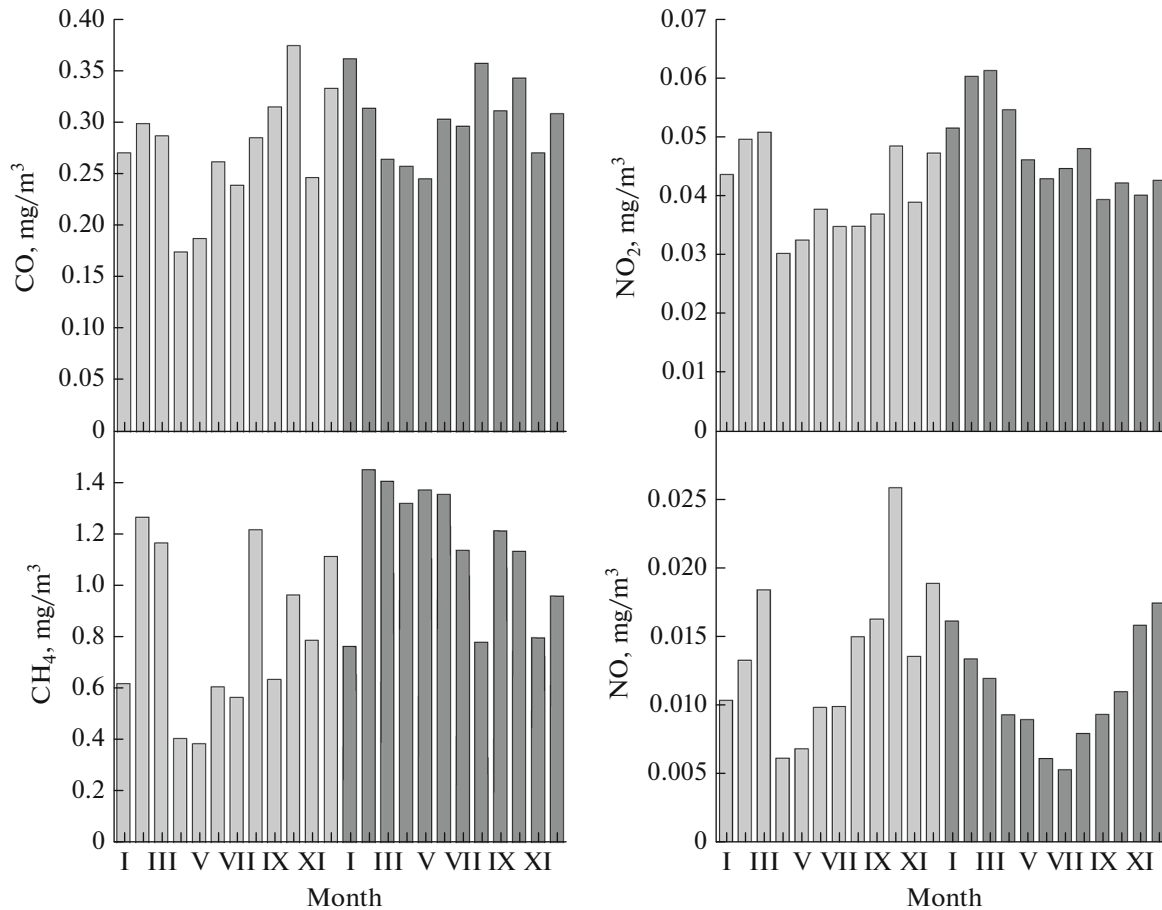
The differences in the distributions of SOC versus temperatures between 2020 and 2021, shown in the



**Fig. 4.** Distribution of the hourly average SOCs for different atmospheric air temperatures in 2020 (black circles) and 2021 (gray circles) at the RUDN station.

diagram, can also indicate lower air pollution of Moscow air in 2020. It can be seen that ozone concentration in the surface atmosphere exponentially increases when air is strongly polluted by ozone precursors at temperatures above  $+30^{\circ}\text{C}$ .

Figure 5 shows the monthly average  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$  concentrations in the surface atmosphere of Moscow in 2020–2021 calculated from monitoring data. It can be seen that April 2020 stands out with a strong reduction of the concentrations of all these gases in air because of the beginning of the lockdown period. The measures were the strictest in April and May. Two months later, the atmospheric pollution level started gradually returning to the prelockdown and even higher values, possibly because industries and motor vehicles had adapted to pandemic conditions. In early 2021, we recorded the concentrations of both carbon-containing substances ( $\text{CO}$  and  $\text{CH}_4$ ) and  $\text{NO}_2$  the largest in that two-year period. The  $\text{CO}$  and  $\text{NO}_2$  contents in early 2021 were  $\sim 30\%$  larger than the average, and the  $\text{CH}_4$  content was  $\sim 70\%$  larger than the average. We turn attention to the specific features of the seasonal  $\text{NO}$  variations in the urban atmosphere, clearly manifested in the diagrams. The concentrations of this substance are minimal in those periods when ozone content is maximal.



**Fig. 5.** Monthly average concentrations of the main surface ozone precursors CO, CH<sub>4</sub>, NO<sub>2</sub>, and NO in the atmosphere in 2020 (light-gray columns) and 2021 (dark-gray columns) at the RUDN station.

## DISCUSSION

Our results show that the high-alert measures taken in Moscow in 2020 in response to the COVID-19 pandemic had led to strong changes in the concentrations of pollutants in the urban atmosphere. That was owing to the reduced total anthropogenic environmental load, because economic activities and the intensity of road and air traffic were significantly reduced in the city. The effect of the general removal of pollutants from Moscow air in this period is difficult to estimate quantitatively; however, the data from monitoring at the RUDN station clearly indicate that the local NO<sub>2</sub>, CO, and CH<sub>4</sub> concentrations decreased by a factor of 1.5 in the surface atmosphere at the center of Moscow at the beginning of pandemic (Fig. 5). The first pandemic year differed little from the statistical average in meteorological conditions. Owing to the reduction of atmospheric air pollution throughout 2020, such a big megalopolises Moscow exhibited quite low concentrations of surface ozone, serving an integrated indicator of the total pollution of atmospheric air in that case [1, 2]. In particular, the concentrations in excess of MPC<sub>m.o</sub>

were observed just once throughout the year. The annual maximum hourly average SOC was 158 µg/m<sup>3</sup>; the annual average SOC was 28 µg/m<sup>3</sup>; and the annual average daily maximal SOC was 55 µg/m<sup>3</sup>. The P80(1h) percentile in the annual distribution of daily maximal SOCs in 2020 had been 76 µg/m<sup>3</sup>. These values can be used subsequently as a target integral index of air quality in Moscow.

The meteorological conditions in Moscow strongly differed between 2020 and 2021. Few heat waves with a maximal daytime temperature of +35°C were observed in summer 2021. (The strong difference between the years consists not only in higher temperature, but also in the heat waves in combination with the blocking anticyclone.) The weather in that period was determined by the blocking anticyclone that ensured rising temperature, air mass stagnation, weak inflow of clean air, and low relative humidity. The anthropogenic environmental load was also higher than in 2020 in view of the softer COVID-19 restrictions. Owing to the totality of these factors, the SOCs, larger than usual, were observed throughout 2021

**Table 1.** Characteristics of SOC time series in Moscow in 2020 and 2021

Parameter	Year	
	2020	2021
Annual average, $\mu\text{g}/\text{m}^3$	28	48
60-minute maximum, $\mu\text{g}/\text{m}^3$	185	482
Daily maximal 60-minute average, $\mu\text{g}/\text{m}^3$	55	101
P80(1h) of annual time series of daily maximal 60-minute values, $\mu\text{g}/\text{m}^3$	76	157
Period of concentrations in excess of $\text{MPC}_{\text{m.o}}$ , h	1	402

starting from spring. In particular, the total period of time when  $\text{MPC}_{\text{m.o}}$  was exceeded by the hourly average SOCs, was 402 h; the annual maximal hourly average SOC was  $482 \mu\text{g}/\text{m}^3$ ; the annual average SOC was  $48 \mu\text{g}/\text{m}^3$ , the annual average daily maximal SOC was  $101 \mu\text{g}/\text{m}^3$ ; and  $\text{P80}(1\text{h}) = 157 \mu\text{g}/\text{m}^3$ . The data are summarized in Table 1 for convenience of comparing the parameters between 2020 and 2021.

It should be noted the ozone concentration of  $\sim 500 \mu\text{g}/\text{m}^3$  was observed last time in Moscow in August 2010, when the maximal daytime temperature exceeded  $42^\circ\text{C}$  [16, 23]. That summer, the urban atmosphere was burdened by smokes from forest fires in the Moscow region. These events are separated by 11 years, which is the time interval close to the solar activity cycle. Additional studies are required to confirm this relationship.

### CONCLUSIONS

In this paper, we presented the results from surface ozone monitoring in the atmosphere of Moscow in 2020 and 2021, under the conditions of economic, motor-vehicle, and social activities reduced due to COVID-19 restrictions. The dynamics of the ozone content in the surface atmosphere is compared between these two years, which differed in both meteorological conditions and the level of the anthropogenic environmental load.

The surface ozone concentrations, relatively low for the megalopolis, were observed throughout 2020 in Moscow. The annual average was  $28 \mu\text{g}/\text{m}^3$ , and the annual maximum was  $185 \mu\text{g}/\text{m}^3$ . This was because cool rainy weather during spring and summer was coupled with low pollutant content in atmospheric air after severe pandemic restrictions were implemented. During summer 2021, several intense heat waves were observed in the megalopolis under the conditions of a blocking anticyclone, when the maximal daytime temperatures reached  $35^\circ\text{C}$ . This, along with higher atmospheric air pollution, as compared to the preceding year, to produce extraordinarily high ozone concentrations. The annual average concentration was  $48 \mu\text{g}/\text{m}^3$ , and the annual maximal concentration was  $482 \mu\text{g}/\text{m}^3$ .

### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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